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Syntheses and Application of Novel Blue Phosphorescent Iridium Complexes to OLEDs

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We synthesized novel iridium complexes having a cyano and/or fluorine-containing phenylpyridine ligands for organic light emitting diodes (OLEDs). The optical properties of these complexes were investigated by ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectrophotometer. The emission color ranges from blue to green depending on the position of substituent groups. One of the complexes, bis[(5-cyano-2-fluorophenyl)-pyridinato- N, C^2] (dipivaloylnate) iridium (III), with the substituent groups on 2 and 5 positions, showed a greenish blue emission peak at 476 nm. The OLED with a structure of glass substrate / indium-tin-oxide (ITO) / tetraphenyl-benzidine-containing poly (arylene ether sulfone) (TPDPES) doped with tris (4-bromophenyl) aminium hexachloro-antimonate (TBPAH) / 2,2'-Bis[3''-(N, N' -ditolylamino) phenyl]biphenyl (3DTAPBP) / iridium complex-doped 2,2'-Bis[4''-(N -carbazole)phenyl]biphenyl (4CzBPB) / 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (t -Bu-TAZ) / lithium fluoride (LiF) / aluminum (Al) exhibited the external quantum efficiency of 17 % and the power efficiency of 33 lm/W at 100cd/m².

Key word: organic light emitting diode, iridium complex, blue emission.

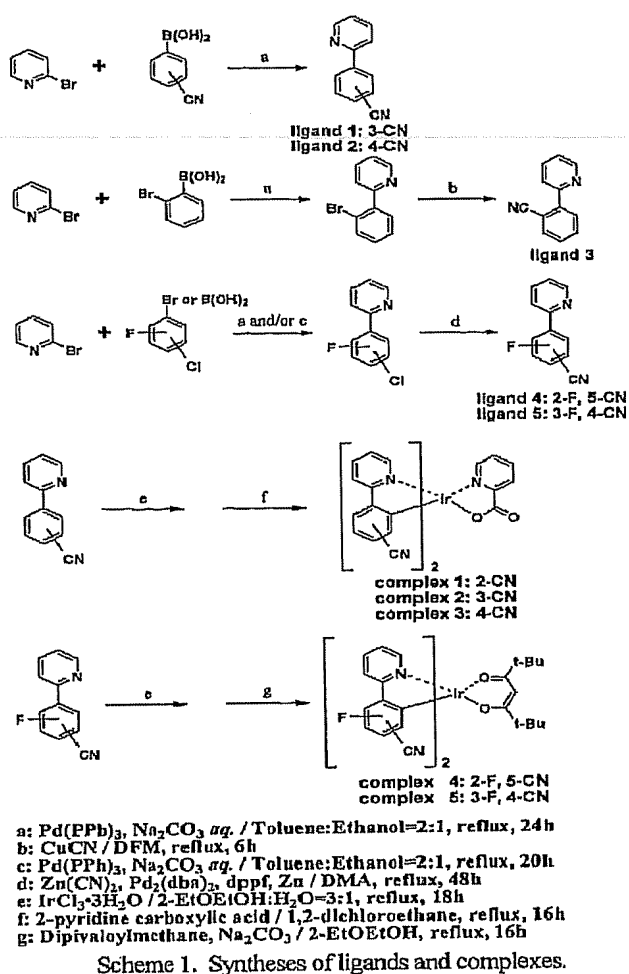
1. Introduction

Lately, there has been a growing interest in OLEDs because they are expected to be the next generation flat panel displays and illumination light sources. Small-size displays using OLEDs have been commercialized and used for cellular phones and car audios [1,2]. For general lighting, however, efficiency and lifetime have to be improved.

In these days, extremely high efficiencies have been achieved by using phosphorescent metal complexes as emitting centers [3,4]. Such high efficiency is due to the fact that light emission occurs from both singlet and triplet

excited states of the complexes. Thus, the internal quantum efficiency could reach 100%. As reported by Adachi et. al., the blue phosphorescent complex, bis[(4,6-difluorophenyl)-pyridinato- N, C^2] (picolinate) iridium (III) (FIrpic), has two fluorine substituents as electron-accepting groups [5, 6].

In this study, novel Ir complexes having fluorine and/or a cyano group as electron-accepting groups were synthesized. The syntheses of the iridium complexes and the characteristics of OLEDs using these complexes will be reported.



2. Experimental

2-1 Syntheses of ligands and complexes

The ligands were synthesized by the reactions of the Negishi coupling, the Suzuki coupling and cyanation as shown in Scheme 1 [7, 8, 9]. The metal complexes were prepared by the reported method [4].

2-1.1 Synthesis of 5-cyano-2-fluorophenyl-2-pyridine (ligand 4)

5-Chloro-2-fluorophenyl-2-pyridine (1.70 g, 8.19 mmol), zinc cyanide (492 mg, 4.91 mmol), bis(dibenzylideneacetone) palladium(0) (147 mg, 0.16 mmol), 1,1'-bis(diphenylphosphino) ferrocene (183 mg, 0.33 mmol), Zn powder (64 mg, 0.98 mmol), and *N,N*-dimethylacetamide (50 ml) were added to a 200-mL

round bottom flask under nitrogen atmosphere. The mixture was refluxed, at 164 °C, and stirred for 48 hrs. Then, it was cooled down to room temperature, followed by the extraction from ethyl acetate (200 ml). The organic phase was washed with ammonium solution (2 N) and brine for 3 times, and dried with sodium sulfate. Finally, the solution was filtered and solvent was removed by vacuum evaporation. The obtained crude material was purified twice by silica gel column chromatography (eluent: ethyl acetate: toluene=1:2 and chloroform). In addition, the solid product was recrystallized from *n*-hexane. Light yellow needle crystals were obtained (510 mg, Yield:31.9 %). $^1\text{H-NMR}$ (270 MHz, CDCl_3 , TMS): δ 8.75 (d, 1H, ArH), δ 8.44 (dd, 1H, ArH), δ 7.83 (m, 2H, ArH), δ 7.69 (dd, 1H, ArH), δ 7.36~7.28 (m, 1H, ArH), δ 7.27 (s, 1H, ArH); IR spectrum (KBr) $-\text{CN}$ (2229 cm^{-1})

2-1.2 Synthesis of bis[(5-cyano-2-fluorophenyl)-pyridinato- N,C^{21}] (dipivaloylnate) iridium(III) (complex 4)

Bis(5-cyano-2-fluorophenyl-2-pyridine) iridium chloro-bridge-dimers (300 mg, 0.24 mmol), dipivaloylmethane (106 mg, 0.58 mmol) and 2-ethoxyethanol (50 ml) were added to a 100-mL round bottom flask under nitrogen atmosphere. The mixture was refluxed at 110 °C and reacted for 16 hrs. Then, the mixture was cooled down to room temperature, and the 2-ethoxyethanol was removed using a vacuum evaporator. The crude product was purified by silica gel column chromatography (eluent: chloroform) for 2 times. The complex was obtained as yellow solid (30 mg, Yield:16.0%). $^1\text{H-NMR}$ (270 MHz, CDCl_3 , TMS): δ 8.35 (d, 2H, ArH), δ 8.28 (dd, 2H, ArH), δ 7.82 (dt, 2H, ArH), δ 7.19~7.13 (m, 4H, ArH), δ 6.75 (dd, 2H, ArH), δ 5.49 (s, 1H, $-\text{CH}_2$), δ 0.80 (s, 18H, $-\text{CH}_3$); IR spectrum(KBr) $-\text{CN}$ (2229 cm^{-1})

2-2 Measurements of UV-vis and PL spectra

The chloroform solutions of the iridium complexes at a concentration of 1.0×10^{-5} mol/l were used for all the measurements. UV-vis absorption and PL spectra were

taken on a UV-2000A spectrophotometer (Shimadzu Co. Ltd.), and a fluoro MAX-2 spectro-photometer (Instruments Co. Ltd.), respectively.

2-3 Fabrication of OLED devices

The molecular structures of organic materials used for device fabrication are listed in Fig.1. TPD PES was supplied by Chemipro Kasei Co. Ltd.. TBP AH and *t*-Bu-TAZ were purchase from Aldrich Co. Ltd. and Dojindo Co. Ltd., respectively, and were used without further purification. The other materials such as 3DTAPBP and 4CzPBP were prepared according to the literature [10]. Other reagents, purchased from Aldrich Co. Ltd., Tokyo Kasei Co. Ltd., and Wako Co. Ltd., were used without further purification.

spin-coated as a hole injection layer on ITO substrate. On the top of the injection layer, 3DTAPBP, as a hole transport layer, iridium complex-doped 4CzPBP as an emitting layer, and *t*-Bu-TAZ as an electron transport layer were vacuum deposited successively at a base pressure of 2.0×10^{-5} Pa. Finally, an electron-injecting layer, LiF and Al cathode were deposited sequentially at 4.0×10^{-5} Pa.

Luminance measurements were carried out with a Topcon BM-8 luminance meter and electroluminescence (EL) spectra were taken by a Hamamatsu photonics PMA-10 optical multi-channel analyzer at room temperature. The phosphorescence spectra of iridium complexes dispersed in poly(methyl metacrylate) (PMMA) were obtained using a streak camera (C4334 from Hamamatsu Photonics) at room temperature.

3. Results and discussions

3-1 Optical properties

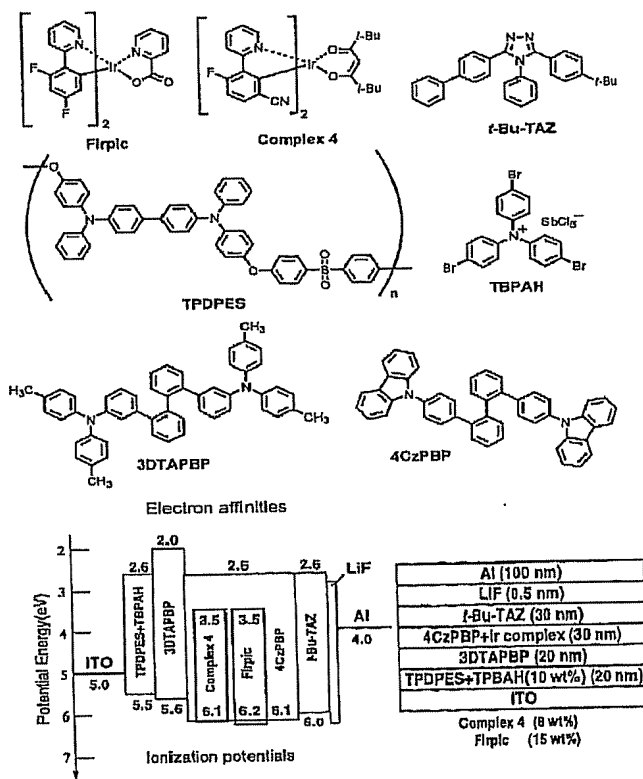


Fig.1. Molecular structures, the energy level diagrams and the configuration of device.

The energy level diagrams and the configuration of device, using complex 4 as the emitting material, are shown in Fig.1. First, TBP AH-doped TPD PES was

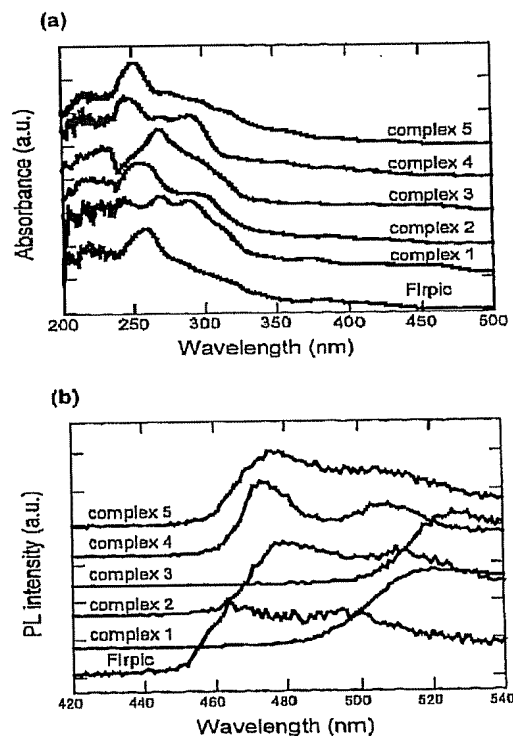


Fig. 2. UV-vis absorption spectra (a), and PL spectra (b) of iridium complexes.

In Fig.2 (a), the absorption bands, ranging from 300 nm to 400 nm, due to the metal-to-ligand-charge-transfer (MLCT) are observed. Fig.2(b) shows the PL spectra of the iridium complexes. Among the complexes, complex 2 exhibits a shorter PL wavelength compared to complexes 1 and 3. The electron density of the carbon atom, coordinating to the central iridium ion, is affected by the position of the substituted cyano group, resulting in the difference in PL spectra. From the phosphorescence decay curves, measured by a streak camera, the complex 4 and Flrpic exhibits similar lifetimes of 1.563 μ s and 1.648 μ s, respectively.

For the device fabrication, complex 4 was used as emitting material because it can be sublimed without decomposition in vacuum.

3-2 Characteristics of OLEDs

OLEDs were fabricated using various concentrations of the emitting materials, complex 4 and Flrpic, in 4CzPBP. The highest efficiencies were obtained at 8wt% for complex 4, and 15wt% for Flrpic, respectively. The difference in the optimized emitter concentration may be due to the difference in the carrier transport properties of the complexes.

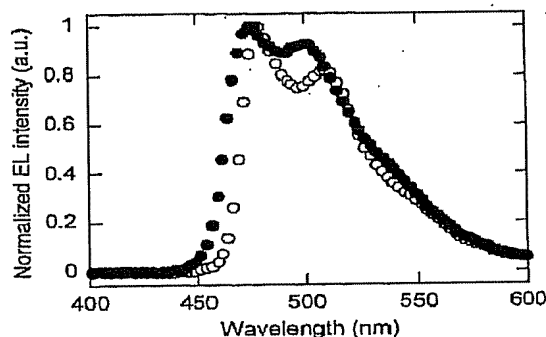


Fig.3. EL spectra of devices with complex 4(○) and Flrpic(●).

An OLED device with complex 4 exhibited greenish blue emission at 477 nm with the CIE (Commission Internationale de l'Eclairage) color coordinates of $x=0.172$, $y=0.456$. And an OLED device based on Flrpic showed sky blue emission peaking at 474 nm with the CIE color coordinates of $x=0.166$, $y=0.395$.

=0.395.

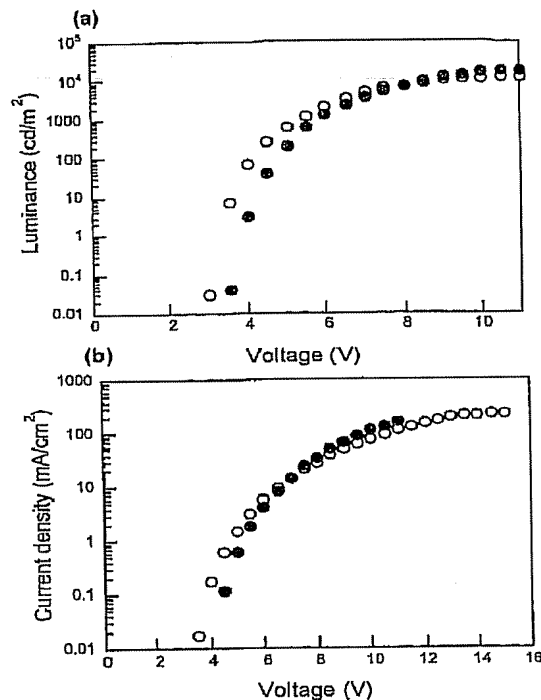


Fig.4. Luminance-voltage (a) and Current density-voltage characteristics (b) of the OLED devices using complex 4(○) and Flrpic(●).

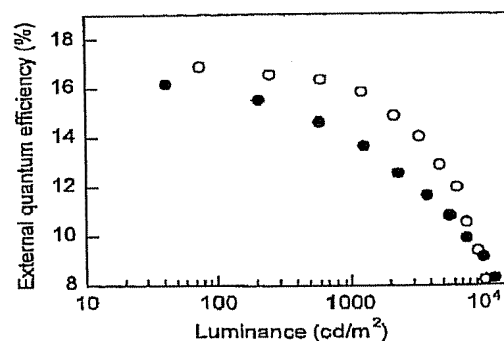


Fig.5 External quantum efficiency-luminance characteristic of the OLED devices using complex 4(○) and Flrpic(●).

Fig.4. shows the luminance-voltage and current density-voltage characteristics of the devices. The device using complex 4 exhibits lower drive voltages compared with those of the device using Flrpic. According to the

energy level diagrams in Fig. 1, the barrier height for the hole injection from the hole transport layer, 3DTAPBP, to the emitter materials is lower for the complex 4 than that for Flrpic due to the lower ionization potential of complex 4.

As shown in Fig. 5, the OLED device based on complex 4 exhibits high external quantum efficiency (EQE). The EQE of 17 % and the luminous efficiency of 33 lm/W are observed at 4.1 V and luminance of 100 cd/m². At 1000 cd/m², the EQE of 16% and the luminous efficiency of 24 lm/W are observed at 5.3 V. On the other hand, a device using Flrpic exhibits the EQE of 16% (24.6 lm/W) and 13.7% (15.6 lm/W) at 100 cd/m² and 1000 cd/m², respectively. Thus, the roll-off in the EQE at higher luminance level is suppressed by the use of complex 4, which is probably due to the wider emission zone resulting from the hole injection to complex 4.

4. Conclusions

In conclusion, we synthesized novel blue emitting iridium complexes, and used as the emitting materials in OLEDs. The OLED device exhibited sky blue emission peaking at approximately 477 nm. High external quantum efficiency of 17% and luminous efficiency of 33 lm/W at 100 cd/m² were observed.

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